

DEMONSTRATION OF A MASS INDEPENDENT ISOTOPIIC FRACTIONATION IN CO REACTION; Mark H. Thiemens and Daniel Meagher, Chemistry Department, B-017, University of California, San Diego, La Jolla California 92093.

The experimental demonstration of chemically produced mass independent isotopic fractionations in oxygen has raised the possibility that the distinct bulk meteoritic oxygen isotopic compositions may be the result of a chemical process. These experiments (1) involved ozone formation from molecular oxygen dissociation, and a mechanism for the process based on isotopic symmetry has been proposed (2) and further tested, using ultraviolet light O₂ photolysis (3). The general nature of the mechanism suggests that reactions such as $^{18}\text{O} + \text{Si}^{16}\text{O}$ and $^{17}\text{O} + \text{Si}^{16}\text{O}$ could feasibly produce the $\delta^{18}\text{O} = \delta^{17}\text{O}$ fractionation and perhaps initiate the gas→solid conversion process.

To determine the possible involvement of mass independent processes in other molecules, experiments were initiated involving the astrophysically relevant molecule CO. Previous experiments (4) reported a mass independent fractionation in a low temperature CO RF discharge. However, oxygen isotopic analyses were done directly on the product CO₂ and were quite poor, due to unknown ¹³C variability. More precise measurements were performed for similar experiments which showed only mass-dependent fractionations (5).

The present experiments subjected pure CO ($\delta^{18}\text{O} = -7.0$, $\delta^{17}\text{O} = -3.6$) to a ~0.5 MHz RF discharge at liquid N₂ temperature (UV light has insufficient flux). Vibrationally excited (CO*) reacts with ground state CO to form CO₂ and C. The CO₂ is cryogenically separated following reaction, converted to CF₄ and O₂ with BrF₅ at 850°C and the O₂ subsequently purified with a molecular sieve at -123°C. The $\delta^{17}\text{O}$, $\delta^{18}\text{O}$ composition was measured on a Finnigan triple collector mass spectrometer with a precision of ~±0.05%. The results are shown in the Figure.

Several important features are present. First, a mass independent fractionation clearly occurs. Second, it is pressure (or energy) dependent and finally, with increasing length of reaction at constant pressure, a secondary mass-dependent fractionation line is produced with heavy isotope enrichment. Note that for a particular pressure a mass fractionation line is defined but offset from the primary mass fractionation line, with the greatest offset at 300 torr. Insufficient data exists to detail the pressure dependency, though relevant experiments are in progress.

It is not clear what the mechanism for the mass independent fractionation step is. If oxygen atoms were present, such as from $\text{CO} + \text{CO}^* \rightarrow \text{C}_2\text{O} + \text{O}$, the symmetry effect may occur in the $\text{O} + \text{CO} \xrightarrow{\text{M}} \text{OCO}$ step. However, this reaction has not been observed to occur. It is well known that under the present experimental conditions a process known as Treanor pumping (6) produces non-Boltzmann heavy isotope enrichments. At low pressures and/or low temperatures (or high $h\nu/kT$), a vibrationally excited species (e.g. CO*) no longer transfers energy by vibration→translation (V→T) exchange, but rather by V→V and V→R (Rotation). Under these conditions, the heavy isotope is preferentially excited. During vibrational energy exchange, $\text{V}_\text{H}^* + \text{V}_\text{H}^0 \rightarrow \text{V}_\text{H}^0 + \text{V}_\text{H}^*$ and $\text{V}_\text{L}^* + \text{V}_\text{L}^0 \rightarrow \text{V}_\text{L}^0 + \text{V}_\text{L}^*$ (where H, L are heavy and light isotopes, and o,* are ground and excited states, respectively), an excited state passes its energy to a ground state species of the same isotope. In addition, $\text{V}_\text{L}^* + \text{V}_\text{H}^0 \rightarrow \text{V}_\text{H}^* + \text{V}_\text{L}^0$ cross exchange occurs, but not $\text{V}_\text{H}^* + \text{V}_\text{L}^0 \rightarrow \text{V}_\text{H}^0 + \text{V}_\text{L}^*$, due to insufficient energy. The net result is preferential population of isotopically heavy vibrationally excited species with the enrichment subsequently carried on to the product CO₂. Carbon monoxide is ideally suited for these exchanges because it has a

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14eV bond strength and is capable of large vibrational energy storage. While Treanor pumping does enrich heavy isotopes and probably occurs in the present experiments, it does not account for the mass independent process.

At present, it is only certain that a pressure (or energy) dependent, mass independent isotopic fractionation occurs in CO self-reaction. The superposition of a secondary mass fractionation requires at least one additional fractionation step. CO self-reaction is of particular interest, since it is observed that the C_2 (carbon dimer) formed in the process is enriched in ^{13}C by 3000‰ at room temperature (7). Since enormous ^{13}C enrichments exist in meteoritic material and CO is a feasible precursor, further experiments on both oxygen and carbon isotopic fractionations will be of interest.

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